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### Permalink

<https://escholarship.org/uc/item/9b2036xv>

### Journal

Journal of Geophysical Research Atmospheres, 101(D1)

### ISSN

0148-0227

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### Publication Date

1996

### DOI

10.1029/95JD02727

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Peer reviewed

## Potential impact of iodine on tropospheric levels of ozone and other critical oxidants

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**Abstract.** A new analysis of tropospheric iodine chemistry suggests that under certain conditions this chemistry could have a significant impact on the rate of destruction of tropospheric ozone. In addition, it suggests that modest shifts could result in the critical radical ratio  $\text{HO}_2/\text{OH}$ . This analysis is based on the first ever observations of  $\text{CH}_3\text{I}$  in the middle and upper free troposphere as recorded during the NASA Pacific Exploratory Mission in the western Pacific. Improved evaluations of several critical gas kinetic and photochemical rate coefficients have also been used. Three iodine source scenarios were explored in arriving at the above conclusions. These include: (1) the assumption that the release of  $\text{CH}_3\text{I}$  from the marine environment was the only iodine source with boundary layer levels reflecting a low-productivity source region, (2) same as scenario 1 but with an additional marine iodine source in the form of higher molecular weight iodocarbons, and (3) source scenario 2 but with the release of all iodocarbons occurring in a region of high biological productivity. Based on one-dimensional model simulations, these three source scenarios resulted in estimated  $\text{I}_x$  ( $\text{I}_x = \text{I} + \text{IO} + \text{HI} + \text{HOI} + 2\text{I}_2\text{O}_2 + \text{INO}_x$ ) yields for the upper troposphere of 0.5, 1.5, and 7 parts per trillion by volume (pptv), respectively. Of these, only at the 1.5 and 7 pptv level were meaningful enhancements in  $\text{O}_3$  destruction estimated. Total column  $\text{O}_3$  destruction for these cases averaged 6 and 30%, respectively. At present we believe the 1.5 pptv  $\text{I}_x$  source scenario to be more typical of the tropical marine environment; however, for specific regions of the Pacific (i.e., marine upwelling regions) and for specific seasons of the year, much higher levels might be experienced. Even so, significant uncertainties still remain in the proposed iodine chemistry. In particular, much uncertainty remains in the magnitude of the marine iodine source. In addition, several rate coefficients for gas phase processes need further investigating, as does the efficiency for removal of iodine due to aerosol scavenging processes.

### Introduction

Of the trace gases in the troposphere, ozone, together with the free radicals generated by its photolysis, is most responsible for defining the oxidizing capacity of the troposphere. Within the troposphere, the mixing ratio of this trace gas is influenced by both transport and photochemical processes [e.g., *Fabian and Pruchniewicz*, 1977; *Mahlman et al.*, 1980; *Chameides and Walker*, 1973; *Fishman and Crutzen*, 1977; *Liu et al.*, 1980]. Conventional thinking suggests that it is the reaction of peroxy radicals, (e.g.  $\text{HO}_2$ ,  $\text{CH}_3\text{O}_2$ , and  $\text{RO}_2$ , where "R" is any organic grouping) with NO to produce the product species  $\text{NO}_2$  that forms the basis of photochemical  $\text{O}_3$  formation. Photolysis of  $\text{NO}_2$

leads to the release of an O atom which, via reaction with  $\text{O}_2$ , results in the formation of one net  $\text{O}_3$  molecule. Photochemical destruction occurs when the  $\text{O}_3$  photolysis product  $\text{O}(^1\text{D})$  reacts with  $\text{H}_2\text{O}$  to produce two hydroxyl radicals, OH, or when hydroperoxyl  $\text{HO}_2$  and OH radicals react with  $\text{O}_3$ . Less certain is the suggestion that halogen species might also provide a photochemical destruction channel for tropospheric  $\text{O}_3$  [e.g., *Chameides and Davis*, 1980; *Singh and Kasting*, 1988; *Barrie et al.*, 1988; *Bottenheim et al.*, 1990; *Chatfield and Crutzen*, 1990; *Keene et al.*, 1990; *Jenkin*, 1993; *Jobson et al.*, 1994; *Le Bras and Platt*, 1995].

Being the most abundant of the halogens, chlorine has undergone the most intense investigation. Both the OH-initiated oxidation of natural and man-made chlorocarbons and the heterogeneous sea-salt reactions have been explored as possible sources of reactive chlorine [e.g., *Singh and Kasting*, 1988; *Keene et al.*, 1990; *Pszenny et al.*, 1993; *Singh*, 1995, and references therein]. However, because of the absence of documented high-altitude sources of chlorine, its high affinity for hydrogen abstraction, and the low reaction probability for converting the product HCl back to reactive chlorine, it now seems unlikely that this halogen by itself represents a significant loss of  $\text{O}_3$ . A possible exception to this conclusion might involve chemistry within

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the marine boundary layer (BL) [Singh *et al.*, this issue]. (The possibility of interhalogen reactions serving as a sink for  $O_3$  is discussed below in the text.)

Investigations of bromine have also focused on the marine BL, but in this case the region of interest has been polar latitudes. Direct measurements of BrO radicals at levels as high as 17 pptv during Arctic springtime conditions [Hausmann and Platt, 1994] have indicated the presence of a significant BL source of reactive bromine. These measurements were also found to coincide with dramatic decreases in ambient ozone levels (e.g., from 40 to <0.5 parts per billion by volume (ppbv)) [Anlauf *et al.*, 1994]. These observations have led to considerable speculation about possible  $O_3$  destruction mechanisms, but in most cases these have been difficult to quantify due to the uncertainties associated with complex heterogeneous sources of bromine [Finlayson-Pitts *et al.*, 1990; McConnell *et al.*, 1992; Fan and Jacob, 1992]. Even so, the polar observations of BrO would seem to suggest that under some conditions, bromine could provide an important BL sink for  $O_3$ .

The impact of iodine in the troposphere, like chlorine and bromine, has also received attention in the context of marine BL chemistry [Chameides and Davis, 1980; Chatfield and Crutzen, 1990; Jenkin *et al.*, 1985; Jenkin, 1993]. More recently, it has been proposed as a sink for  $O_3$  in the lower stratosphere [Solomon *et al.*, 1995]. Unlike bromine and chlorine, the production of reactive iodine requires no complex heterogeneous mechanism. For example, of the companion methyl halides,  $CH_3I$  is the only species that readily photolyzes within the troposphere. In fact, its photochemical lifetime is roughly 4 to 5 times shorter than the most photosensitive bromine compound  $CHBr_3$ .

The objective of this study will be to reexamine the role of iodine as a tropospheric sink for  $O_3$  and to also explore its ability to modulate the centrally important radical ratios  $HO_2/OH$  and  $NO_2/NO$ . This analysis has been motivated by both the availability of new  $CH_3I$  data for the middle and upper free troposphere and the updated values for several critical photochemical/gas kinetic rate coefficients. The  $CH_3I$  observations are the first of their kind and were recorded as part of NASA's western Pacific Exploratory Mission (PEM-West A).

## 2. Iodine Sources and Transport

### 2.1 Marine Observations of Iodine

As previously reviewed by Chameides and Davis [1980], there is now ample evidence showing that the methyl halide  $CH_3I$  is a metabolic byproduct of many species of marine algae. This iodocarbon alone was estimated to provide a global source of iodine of the order of 1-2 Tg/yr. By comparison, industrial sources of volatile iodine were indicated to be less than 10% of the natural biogenic source. Yet other marine sources such as the direct photolysis of iodine compounds in ocean surface waters were listed as potentially important but still nonquantifiable.

More recently, Solomon *et al.* [1995] have provided an update of global marine iodine sources. The most significant additions have been those reported by Moore and Tokarczyk [1992], Klick and Abrahamsson [1992], and Schall and Heumann [1993]. Collectively, these investigators' observations indicate that the source strength for other iodocarbons (e.g.,  $CH_2I_2$ ,  $C_2H_5I$ , and  $CH_2ICl$ ) could possibly

exceed that for  $CH_3I$ . For example, Schall and Heumann's measurements in the Arctic suggest that  $CH_3I$  may only represent 26% of the total marine iodine released to the atmosphere. (Note that because of an expected red shift in the absorption spectrum for species such as  $CH_2I_2$  and  $C_2H_5I$  relative to  $CH_3I$ , one would expect the lifetimes for these species to be even shorter than that for  $CH_3I$ .)

Atmospheric measurements of  $CH_3I$  have primarily been confined to the marine BL with average mixing ratios ranging from 1 to 3 pptv [Liss and Slater, 1974; Singh *et al.*, 1983; Rasmussen *et al.*, 1982; Reifenhauer and Heumann, 1992]; but for regions characterized as having high biological productivity, much higher mixing ratios have been reported (i.e., 10-20 pptv), with one recent observation in the coastal waters of England reaching as high as 43 pptv [Oram and Penkett, 1994]. Marine areas nominally labeled as high-productivity regions are those typically found at high latitudes during springtime or those characterized as experiencing marine upwelling. In the latter regard, the equatorial upwelling in the Pacific could define an important area for the atmospheric influence of iodine. This conclusion reflects the fact that not only would this region be a potentially rich source of iodine but also would be a region that experiences considerable deep convection.

As noted earlier in the text, the  $CH_3I$  observations recorded during PEM-West A are unique in that both marine BL and free tropospheric measurements were recorded. These measurements were based on whole air samples collected with preconditioned stainless steel canisters. The contents were typically analyzed within 7 days using standard gas chromatograph (GC)/electron capture analysis techniques [Blake *et al.*, 1994, this issue]. Among the problems that may have impacted on the integrity of these samples was the extremely dry conditions (i.e., specific humidity <2 g/kg) experienced in the upper troposphere. Previous experience has shown that in some cases, loss of halocarbons to canister walls could occur. (Following PEM-West A, it was determined that adding 5 torr of purified  $H_2O$  prior to use typically alleviated the above problem.) Since there have been no previous studies indicating increases of  $CH_3I$  during storage, this suggests that the results reported here most likely represent a lower limit to the true  $CH_3I$  level.

Two different calibration methods were used in an effort to establish the accuracy of the reported  $CH_3I$  measurements. In the first approach to verify the dilution procedure, a low pptv  $CH_3Br$  standard, prepared by NIST, was compared against  $CH_3I$  and  $CH_3Br$  standards made from each of the pure compounds. In addition, permeation tubes for methyl iodide and methyl bromide were diluted in ultrapure air as a means of calibrating working reference gases. Good agreement was observed between the two methods. To estimate the precision of the  $CH_3I$  measurements, 11 samples collected consecutively during a BL run and 7 consecutive samples collected around 7 km were analyzed. For the BL run the results were  $1.3 \pm 0.08$ ; whereas, at 7 km the mean and standard deviation were  $0.13 \pm 0.03$  pptv. (A more detailed description of the analytical technique used in the analysis of methyl halides can be found in the work of T.-Y. Chen *et al.*, manuscript in preparation, 1996.)

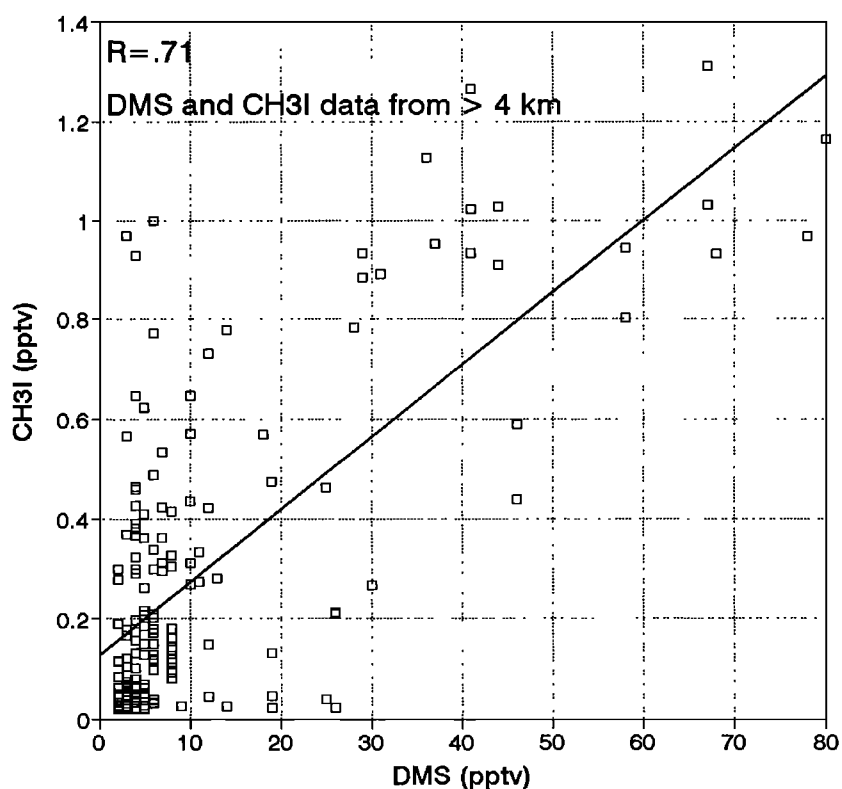
As still a further check on the reliability of these field data, we have compared the observed PEM-West A values for dimethyl sulfide (DMS) against those of  $CH_3I$ . (We note here that the GC-mass spec technique used during PEM West

A to measure DMS included independent calibration runs for each individual measurement of DMS.) Since both compounds have predominantly marine sources, to a first approximation one might expect that the ratio of concentration for these two species should be similar at both high and low altitudes, provided their atmospheric lifetimes were not too dissimilar. In fact, at low altitudes some difference exists because DMS is controlled by OH oxidation and  $\text{CH}_3\text{I}$  by photolysis (e.g., DMS <1 day versus  $\text{CH}_3\text{I}$  3–4 days); whereas at upper free tropospheric altitudes, reduced levels of OH and an enhanced UV flux result in nearly the same lifetime (i.e., ~2 days). For the PEM West A data set, a comparison of matched BL observations of DMS and  $\text{CH}_3\text{I}$  (all above the limit of detection) gave a median ratio value for DMS/ $\text{CH}_3\text{I}$  of 25. By comparison, for the highest-altitude data blocks, the value of this ratio was estimated at 43. Given the shift in lifetimes with altitude, one might actually expect that the high-altitude ratio should have been lower than that at low altitudes. However, upon reflecting on the fact that frequently there was a high degree of natural variability in the levels of both species and that the sampling integration times differed significantly (e.g., DMS, 3–4 min;  $\text{CH}_3\text{I}$ , 10–60 s), one could argue that the level of agreement cited above still suggests that the high-altitude measurements of  $\text{CH}_3\text{I}$  were probably not seriously compromised. Further evidence supporting this conclusion can be found in the level of correspondence between the DMS and  $\text{CH}_3\text{I}$  measurements shown in Figure 1. This figure shows a scatterplot of these two species under conditions for which their lifetimes would be somewhat similar, i.e., data recorded for altitudes above 4 km. In this case a regression analysis, based on data taken from all latitudes, gave a Pearson R correlation coefficient of

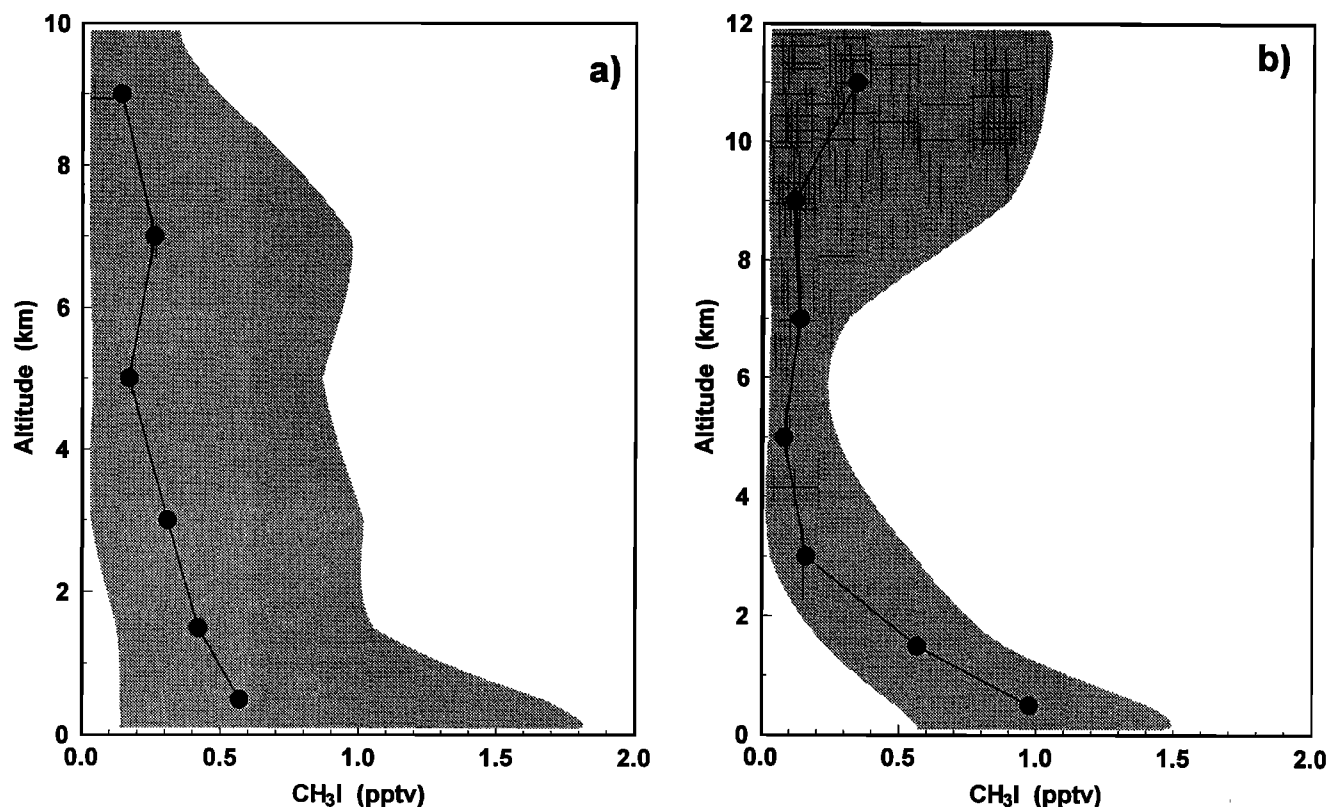
0.71. Still the possibility of "offset" errors cannot be totally ruled out. At this time, therefore, our assessment is that the  $\text{CH}_3\text{I}$  measurements are probably good to within a factor of 2 to 3.

The range and median values for the  $\text{CH}_3\text{I}$  observations recorded during PEM-West A are shown in Figures 2a and 2b. These data have been binned every 2 km except for low altitudes where the height was confined to 1 km. In addition, both the upper and the lower 5% of the observations have been trimmed in the "range" display. The latitudinal zones shown are those designated elsewhere as "western tropical North Pacific,"  $0^\circ$ – $18^\circ\text{N}$ , and "western North Pacific rim,"  $18^\circ$ – $42^\circ\text{N}$ . This division reflects the PEM-West A  $\text{O}_3$  tendency analysis reported by Davis *et al.* [this issue].

The data displayed in Figures 2a and 2b show marine BL values of  $\text{CH}_3\text{I}$  reaching as high as 1.5 to 1.8 pptv. For the tropics these levels are then observed to decrease to < 0.5 pptv. In contrast to the tropics, the Pacific rim data reveal the presence of many elevated  $\text{CH}_3\text{I}$  observations at high altitude, with values at 10–12 km reaching >1 pptv. These high-altitude values reflect the influence of observations recorded during PEM-West A flight 9. This mission was unique in that the flight profile was designed to sample the low-altitude inflow and high-altitude outflow from Typhoon Mireille. The strong vertical pumping action from this typhoon produced enhanced high-altitude levels of both  $\text{CH}_3\text{I}$  as well as DMS [Newell *et al.*, this issue; Thornton *et al.*, this issue] Median values of  $\text{CH}_3\text{I}$  are seen to range from highs of 0.6 to 1 pptv in the marine BL to lows of 0.1 to 0.15 at middle and high-altitudes. The Pacific rim region is seen as having the largest range in median values (e.g., 1 to 0.1 pptv) with the minimum coming at middle altitudes. The



**Figure 1.** Scatterplot of  $\text{CH}_3\text{I}$  versus DMS. Data have been restricted to simultaneous measurements of  $\text{CH}_3\text{I}$  and DMS above 4 km. The solid line indicates the best fit to the data.



**Figure 2.** Altitude distributions for  $\text{CH}_3\text{I}$  as measured during PEM-West A for the latitude ranges: (a)  $0^\circ$ - $18^\circ\text{N}$  and (b)  $18^\circ$ - $42^\circ\text{N}$ . Circles indicate the median values for altitude bins: 0-1 km, 1-2 km, 2-4 km, 6-8 km, 8-10 km, and 10-12 km. Shaded regions indicate the range of  $\text{CH}_3\text{I}$  observations within each bin after trimming the upper and lower 5% of the data within each bin.

resulting hour glass shaped profile is thus seen to be similar to those for several other PEM-West A trace gases whose distributions were strongly influenced by deep convection [e.g., Blake *et al.*, this issue]. By contrast, in the tropics, although BL values start lower (i.e., 0.6 pptv), a rather steady roll-off in  $\text{CH}_3\text{I}$  median values occurs from the BL to altitudes of 8-10 km, resulting in a high-altitude median value of  $\sim 0.15$  pptv.

## 2.2. Vertical Transport and $\text{I}_x$ Distributions

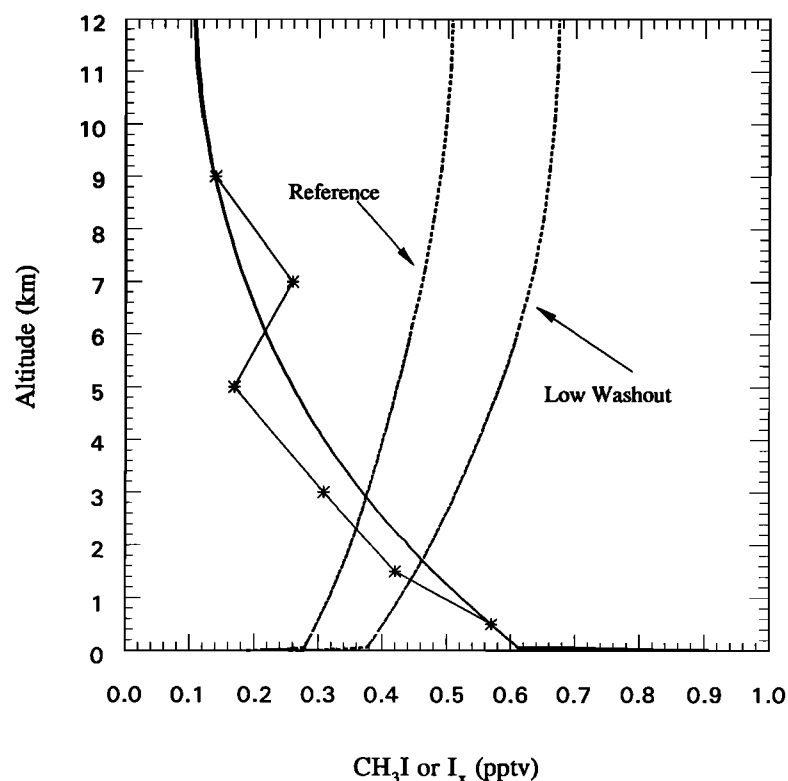
As discussed below in the text with reference to the photochemistry of tropospheric iodine, the abundance of total reactive iodine  $\text{I}_x$  ( $\text{I}_x = \text{I} + \text{IO} + \text{HOI} + \text{HI} + 2\text{I}_2\text{O}_2 + \text{INO}_x$ ) in the middle and upper troposphere has been assessed in terms of a photochemical source, e.g., photolysis of  $\text{CH}_3\text{I}$  and/or other iodocarbons, and losses in the form of surface deposition and heterogeneous uptake by cloud droplets, precipitation, and possibly aerosols. Thus given the stochastic nature of these loss processes in the middle and upper troposphere, one can estimate that the timescales involved could be significantly longer than that for vertical transport. We have investigated this question in this study by using a simple one-dimensional model [McKeen *et al.*, 1989] that incorporates a first-order diffusion process to describe vertical transport.

A particular concern in employing the one-dimensional formulation is that it is difficult to envision how such a

representation might adequately simulate deep convective processes that obviously are a major contributor to the relatively high mixing ratios of  $\text{CH}_3\text{I}$  in the upper troposphere. In this regard we have assumed that the entrainment and detrainment of air by convective processes has been effective at nearly all altitudes. In other words, the combination of deep and shallow convection effectively mix boundary layer air to various altitudes. Moreover, we assume that the ensemble of air masses sampled during PEM-West A were representative of the ambient environment. As discussed in the above text, for the case of the tropics an examination of the median profile of  $\text{CH}_3\text{I}$  (e.g., Figure 2a) as well as that of DMS does show a gradual decrease with altitude. Thus this is consistent with the above assumptions, and suggests that the median profile can be simulated with the eddy diffusion formulation.

For this investigation a single value of the diffusion coefficient ( $K_z$ ) was used from 50 meters above the surface to the highest altitudes of the model at 12 km. Below 50 m a very stable layer was assumed with  $\text{I}_x$  being immediately deposited at the surface upon contact. The initial concentrations of  $\text{I}_x$  and  $\text{CH}_3\text{I}$  were assumed to be zero. An integration time of 20 days was chosen so as to permit  $\text{CH}_3\text{I}$  to reach a steady state condition at high-altitudes.

The key features of this one-dimensional transport simulation are illustrated in Figure 3. Also shown are the median values estimated for  $\text{CH}_3\text{I}$  as given in Figure 2a. With photolysis acting as the only loss mechanism for  $\text{CH}_3\text{I}$ ,



**Figure 3.** Altitude profiles of  $\text{CH}_3\text{I}$  and  $\text{I}_x$  based on one-dimensional model simulations. Asterisks indicate the median values of  $\text{CH}_3\text{I}$  for the PEM-West A tropical zone  $0^\circ\text{--}18^\circ\text{N}$ . The solid line indicates the simulated profile for  $\text{CH}_3\text{I}$  assuming an emission flux of  $2 \times 10^{11}$  molecules/ $\text{m}^2/\text{s}$  and an eddy diffusion coefficient  $K_z$  of  $80 \text{ m}^2/\text{s}$ . Dotted lines indicate  $\text{I}_x$  levels for: (1)  $K_z$  value of  $80 \text{ m}^2/\text{s}$  and washout rates according to Table 1, ("reference" curve), and (2)  $K_z$  value of  $80 \text{ m}^2/\text{s}$  with washout rates from Table 1 decreased by one half below 5 km and zero for altitudes above 5 km ("low washout").

a reasonable fit to the  $\text{CH}_3\text{I}$  experimental observations was found when  $K_z$  was assigned a value of  $80 \text{ m}^2/\text{s}$  and the surface emission rate was given a value of  $2 \times 10^{11}$  molecules/ $\text{m}^2/\text{s}$ . In this case, the value of  $K_z$ , relative to the photolysis loss rate, defines the vertical gradient for  $\text{CH}_3\text{I}$ , while the flux value simply shifts the vertical profile along the abscissa. We note that our value for  $K_z$  of  $80 \text{ m}^2/\text{s}$  is only slightly larger than the value used by *Liu et al.* [1984] (i.e.,  $50\text{--}70 \text{ m}^2/\text{s}$ ). These authors based their value on observations of  $^{222}\text{Rn}$  over the continental United States during summertime. Like  $\text{CH}_3\text{I}$ , the tracer  $^{222}\text{Rn}$  has only a surface source and during the summer season is probably also dynamically forced by convection to high-altitudes.

The  $\text{I}_x$  "reference" profile shown in Figure 3 was obtained using the same  $K_z$  value together with an altitude dependent washout rate for all soluble species as defined by *Logan et al.* [1981] (see Table 1). The resulting  $\text{I}_x$  profile shows a maximum of  $\sim 0.5$  pptv for altitudes approaching 12 km. To explore the magnitude of influence of the assumed value for the washout rate on  $\text{I}_x$ , a simulation was also carried out in which this rate was reduced by a factor of  $1/2$  for altitudes below 5 km and to zero above 5 km. As shown in Figure 3,  $\text{I}_x$  is enhanced by only 0.2 pptv, yielding a maximum value of 0.7 pptv. The effect resulting from assuming a much faster  $\text{I}_x$  removal rate than that employed for the "reference" profile is discussed below in the text.

For purposes of exploring the tropospheric impact of iodine in this investigation, we have selected three  $\text{I}_x$  source

scenarios. The low scenario, involving 0.5 pptv of  $\text{I}_x$  at 10 km, assumes  $\text{CH}_3\text{I}$  to be the only source of iodine and uses the "reference" value of  $K_z$  of  $80 \text{ m}^2/\text{s}$  and a  $\text{CH}_3\text{I}$  flux of  $2 \times 10^{11}$  molecule/ $\text{m}^2/\text{s}$ , e.g. low productivity marine water. A somewhat more realistic scenario, we believe, is one involving 1.5 pptv of  $\text{I}_x$  which reflects the inclusion of source compounds like  $\text{CH}_2\text{I}_2$  and  $\text{C}_2\text{H}_5\text{I}$  that could more than double the iodine flux to the atmosphere. The final scenario explored here involves a high-altitude value of  $\text{I}_x$  of 7 pptv. This scenario considers possibilities such as  $\text{CH}_3\text{I}$  defining only 26% of the marine iodine flux to the troposphere (see earlier discussion of iodine sources), lower loss rates for  $\text{I}_x$ , and higher marine primary productivity relative to that observed during PEM-West A. We note that vertical profiles of  $\text{I}_x$  for scenarios 2 and 3 were obtained here by scaling the above cited 10-km values according to the  $\text{I}_x$  reference profile in Figure 3.

### 3. Tropospheric Iodine Chemistry and Model Results

#### 3.1 Description of Model

The basic photochemical model used in this study is similar to that described by *Davis et al.* [this issue], *Crawford et al.* [this issue], and *Davis et al.* [1993]. Iodine chemistry was added to this basic model as per the reactions shown in Table 1. Once the level of  $\text{I}_x$  was established, as per the discussion in the above text, the partitioning of  $\text{I}_x$  and

**Table 1.** Tropospheric Iodine Reactions in the Evaluation of Iodine Photochemistry

Reaction	J or K Values	Reference
(R1) $\text{CH}_3\text{I} + h\nu \rightarrow \text{CH}_3 + \text{I}$	$7.9 \times 10^{-6} \text{ }^a$	cross sections from <i>Calvert and Pitts</i> [1963]
(R2) $\text{I} + \text{O}_3 \rightarrow \text{IO} + \text{O}_2$	$2.0 \times 10^{-11} \exp(-890/T)$	<i>Atkinson et al.</i> [1993]
(R3) $\text{I} + \text{HO}_2 \rightarrow \text{HI} + \text{O}_2$	$1.5 \times 10^{-11} \exp(-1090/T)$	<i>Atkinson et al.</i> [1993]
(R4) $\text{I} + \text{NO}_2 + \text{M} \rightarrow \text{INO}_2 + \text{M}$	$k_0 = 3.0 \times 10^{-31} (T/300)^{-1} [\text{N}_2]^b$ $k_{\text{inf}} = 6.6 \times 10^{-11}$ $F_0 = [\exp(-T/650) + \exp(-2600/T)]$	<i>Atkinson et al.</i> [1993]
(R5) $\text{INO}_2 + h\nu \rightarrow .5(\text{I} + \text{IO} + \text{NO} + \text{NO}_2)$	$2.9 \times 10^{-3}$	assumed same as $\text{IONO}_2 + h\nu$
(R6) $\text{IO} + h\nu \rightarrow \text{I} + \text{O}$	$2.2 \times 10^{-1} \text{ }^a$	cross sections from <i>Stickel et al.</i> [1990] and <i>Laszlo et al.</i> [1995]
(R7) $\text{IO} + \text{NO} \rightarrow \text{I} + \text{NO}_2$	$7.3 \times 10^{-12} \exp(330/T)$	<i>Atkinson et al.</i> [1993]
(R8) $\text{IO} + \text{HO}_2 \rightarrow \text{HOI} + \text{O}_2$	$8.4 \times 10^{-11}$	<i>DeMore et al.</i> [1994]
(R9) $\text{IO} + \text{IO} \rightarrow 2(\text{I} + \text{O}_2) + .8(\text{I}_2\text{O}_2)$	$1.7 \times 10^{-12} \exp(1020/T)$	<i>Atkinson et al.</i> [1993]/ products <i>Jenkin et al.</i> [1985]
(R10) $\text{IO} + \text{NO}_2 + \text{M} \rightarrow \text{IONO}_2 + \text{M}$	$k_0 = 7.7 \times 10^{-31} (T/300)^{-5} [\text{N}_2]^b$ $k_{\text{inf}} = 1.6 \times 10^{-11}$ $F_0 = 0.4$	<i>Atkinson et al.</i> [1993]
(R11) $\text{IONO}_2 + h\nu \rightarrow .5(\text{I} + \text{IO} + \text{NO}_2 + \text{NO}_3)$	$2.9 \times 10^{-3} \text{ }^a$	cross sections from <i>Atkinson et al.</i> [1993] products assumed, this work
(R12) $\text{IONO}_2 \rightarrow \text{IO} + \text{NO}_2$	$2.07 \times 10^{-15} \exp(-11859/T)$	<i>Chatfield and Crutzen.</i> [1990]
(R13) $\text{HI} + \text{OH} \rightarrow \text{I} + \text{H}_2\text{O}$	$3.0 \times 10^{-11}$	<i>Atkinson et al.</i> [1993]
(R14) $\text{HOI} + h\nu \rightarrow \text{I} + \text{OH}$	$5.9 \times 10^{-3} \text{ }^a$	cross sections from <i>Atkinson et al.</i> [1993]
(R15) $\text{HOI} + \text{OH} \rightarrow \text{IO} + \text{H}_2\text{O}$	$2.0 \times 10^{-13}$	<i>Chameides and Davis</i> [1980]
(R16) $\text{I}_2\text{O}_2 + h\nu \rightarrow 2\text{I} + \text{O}_2$	$1.3 \times 10^{-2} \text{ }^a$	assumed $9 \times (\text{Cl}_2\text{O}_2 + h\nu)$ cross sections from <i>DeMore et al.</i> [1994]
(R17) $\text{HI} \rightarrow \text{deposition}$	$1.16 \times 10^{-5}$	estimated
(R18) $\text{HOI} \rightarrow \text{deposition}$	$1.16 \times 10^{-5}$	estimated
(R19) $\text{I}_2\text{O}_2 \rightarrow \text{deposition}$	$1.16 \times 10^{-5}$	estimated
(R20) $\text{HI} \rightarrow \text{rainout/washout}$	see footnote c	<i>Logan et al.</i> [1981]
(R21) $\text{HOI} \rightarrow \text{rainout/washout}$	see footnote c	<i>Logan et al.</i> [1981]
(R22) $\text{I}_2\text{O}_2 \rightarrow \text{rainout/washout}$	see footnote c	<i>Logan et al.</i> [1981]
(R23) $\text{HI} \rightarrow \text{aerosol}$	see text	estimated
(R24) $\text{HOI} \rightarrow \text{aerosol}$	see text	estimated
(R25) $\text{I}_2\text{O}_2 \rightarrow \text{aerosol}$	see text	estimated

<sup>a</sup>Photolysis rates have been calculated for a solar zenith angle of 30° at the surface.

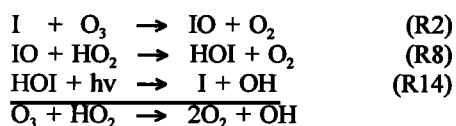
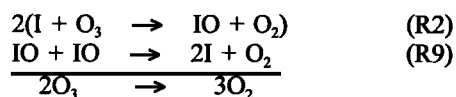
<sup>b</sup> $k = (k_0 k_{\text{inf}} / (k_0 + k_{\text{inf}})) F_0$ .

<sup>c</sup> $2.31 \times 10^{-6}$  (0–4 km),  $2.31 \times 10^{-6} \exp(1.6-4z)$  (4–12 km).

the interaction of iodine species with  $\text{O}_3$  and other  $\text{HO}_x$  species was defined by our iodine-modified box model.

Figure 4 shows our current iodine chemistry in schematic form, thus illustrating the extensive cycling among the individual iodine species I, IO,  $\text{I}_2\text{O}_2$ , HOI, and  $\text{INO}_x$ . Model-estimated vertical profiles for each of these species are shown in Figure 5. These profiles are based on a high-altitude  $\text{I}_x$  level of 1.5 pptv. They tend to show that at all altitudes but 8–10 km, HOI is the dominant iodine species. For the latter altitude range, the concentration levels of I, HI, IO, and HOI are seen to all lie within a factor of 2.5 of each other. By comparison, the species  $\text{I}_2\text{O}_2$ ,  $\text{INO}_2$ , and  $\text{IONO}_2$  are 1 to 2 orders of magnitude lower in concentration.

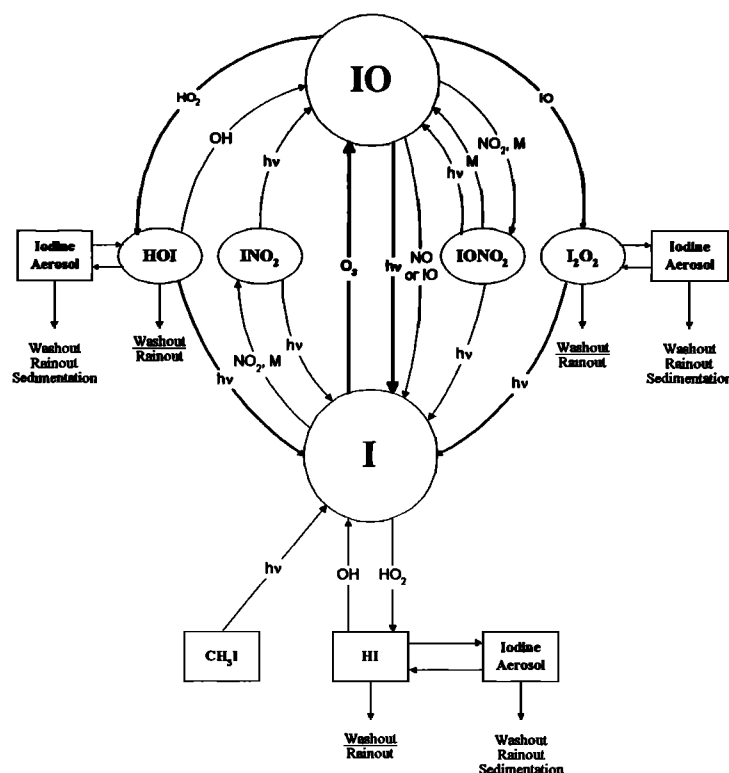
From a detailed analysis of the chemistry presented in Figure 4, two  $\text{O}_3$  destruction sequences can be identified:



Quite noteworthy here is that the rate-controlling step in each sequence involves the reaction of IO, either with itself or with  $\text{HO}_2$ . In this regard, the proposed iodine chemistry differs from that outlined for the lower stratosphere by *Solomon et al.* [1995]. These investigators have suggested that interhalogen/IO reactions involving BrO and ClO radicals were probably the dominant  $\text{O}_3$  loss processes in the lower stratosphere. This reflects the fact that *Solomon et al.* [1995] estimate much higher levels of bromine and chlorine for the lower stratosphere than those predicted by our standard model for the upper troposphere. In our standard model only gas phase species such as  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Cl}_2$ , and  $\text{C}_2\text{Cl}_4$  have been considered as sources of  $\text{Cl}_x$ . This results in only a few pptv of  $\text{Cl}_x$ , most of which is tied up in the form of HCl and therefore of little chemical consequence.

To further explore the possible importance of interhalogen chemistry in the upper troposphere, we have examined two other possible  $\text{Cl}_x$  sources. The first of these considered transport of a  $\text{Cl}_x$  source from the stratosphere. An upper limit to the amount of  $\text{Cl}_x$  from this source can be estimated by assuming that both  $\text{O}_3$  and  $\text{Cl}_x$  are inert tracers in the lower stratosphere and upper troposphere. We believe this should be a reasonably good assumption for  $\text{O}_3$  as its production and loss rates are very small [e.g., *Davis et al.*, this issue]. For  $\text{Cl}_x$ , one would intuitively expect that soluble

## Tropospheric Iodine Photochemical Reaction Scheme



**Figure 4.** Tropospheric iodine photochemical reaction scheme. The relative flux strength for each pathway is indicated by the width of each connecting line. Stable species are those shown as rectangles. Short-lived species are indicated as circles and ellipses.

species like HCl would be effectively scavenged by high-altitude clouds. However, extensive observations of similar species (i.e.,  $\text{NO}_y$ ) suggests that it might tend to behave as if it were nearly inert [e.g., Murphy *et al.*, 1993; Liu *et al.*, this issue; and Smyth *et al.*, this issue]. Given that the assumption of inertness of  $\text{Cl}_x$  and  $\text{O}_3$  is correct, the ratio  $\text{Cl}_x/\text{O}_3$  should be approximately constant for the lower stratosphere and upper troposphere. Thus using values near 20 km [World Meteorological Organization (WMO), 1989], we have estimated a value for  $\text{Cl}_x/\text{O}_3$  of  $\sim 5 \times 10^{-4}$ . For the tropical zone  $0^\circ$ – $18^\circ\text{N}$ , where the median level of  $\text{O}_3$  was 32 ppbv, this gives an estimated value for the mixing ratio of  $\text{Cl}_x$  of 16 pptv. Similarly, for the Pacific rim region ( $18^\circ$ – $42^\circ\text{N}$ ) where the median value of  $\text{O}_3$  was 45 ppbv, the estimated mixing ratio for  $\text{Cl}_x$  would be 23 pptv. Thus we estimate that these  $\text{Cl}_x$  levels could provide no more than a  $10^5$  molecules/ $\text{cm}^3$  source of ClO, assuming only gas phase chemistry to be important. At this level the concentration is more than 2 orders of magnitude less than that for  $\text{HO}_2$  and hence would render any interhalogen  $\text{O}_3$  sink reaction unimportant.

The other high-altitude source of  $\text{Cl}_x$  considered here involves the reaction of sulfuric or nitric acid with sea-salt aerosols, the latter being transported to the upper troposphere via deep convection. This source, together with HCl released from the gas phase oxidation of chlorocarbons (see above text), has been suggested as a possible contributor to the 400 pptv levels of HCl reported for the tropical tropopause by Tuck *et al.* [1995]. Our assessment of this alternate source suggests that if only gas phase chemistry is invoked, the

resulting ClO level gives a rate for the  $\text{IO} + \text{ClO}$  ozone sink reaction that is still only a few percent of that for (R8). Thus we conclude that if interhalogen  $\text{O}_3$  sink reactions are to be important in the troposphere, a significant yet unidentified source of reactive chlorine will need to be found. This could potentially be some form of heterogeneous process which might not only release chlorine but also bromine.

Although some uncertainty still remains concerning aspects of the gas phase chemistry of iodine, the issue of  $\text{I}_x$  heterogeneous reactions encompasses perhaps an even greater uncertainty. As indicated in Table 1, washout/rainout and surface deposition are major components of the current model. In the marine BL this results in an approximate 1-day lifetime for  $\text{I}_x$ . By comparison, for middle free tropospheric altitudes these processes lead to an  $\text{I}_x$  lifetime that ranges from 5 to 10 days, thus being comparable to that for reasonably fast vertical mixing. For the upper free troposphere, as evaluated by equations 20–23, washout/rainout rates are factors of 5 to 15 times slower than vertical mixing. Thus further enhancements in the removal rate due to microphysical processes operating within deep convection or, alternatively, to other noncloud related aerosol heterogeneous losses could potentially lead to significant decreases in the high-altitude levels of  $\text{I}_x$ . To explore this possibility, simulations were carried out using the previously described one-dimensional model in which removal times of 7 and 14 days were assumed. The results showed that  $\text{I}_x$  was decreased at the highest altitudes by 50% and 30%, respectively.



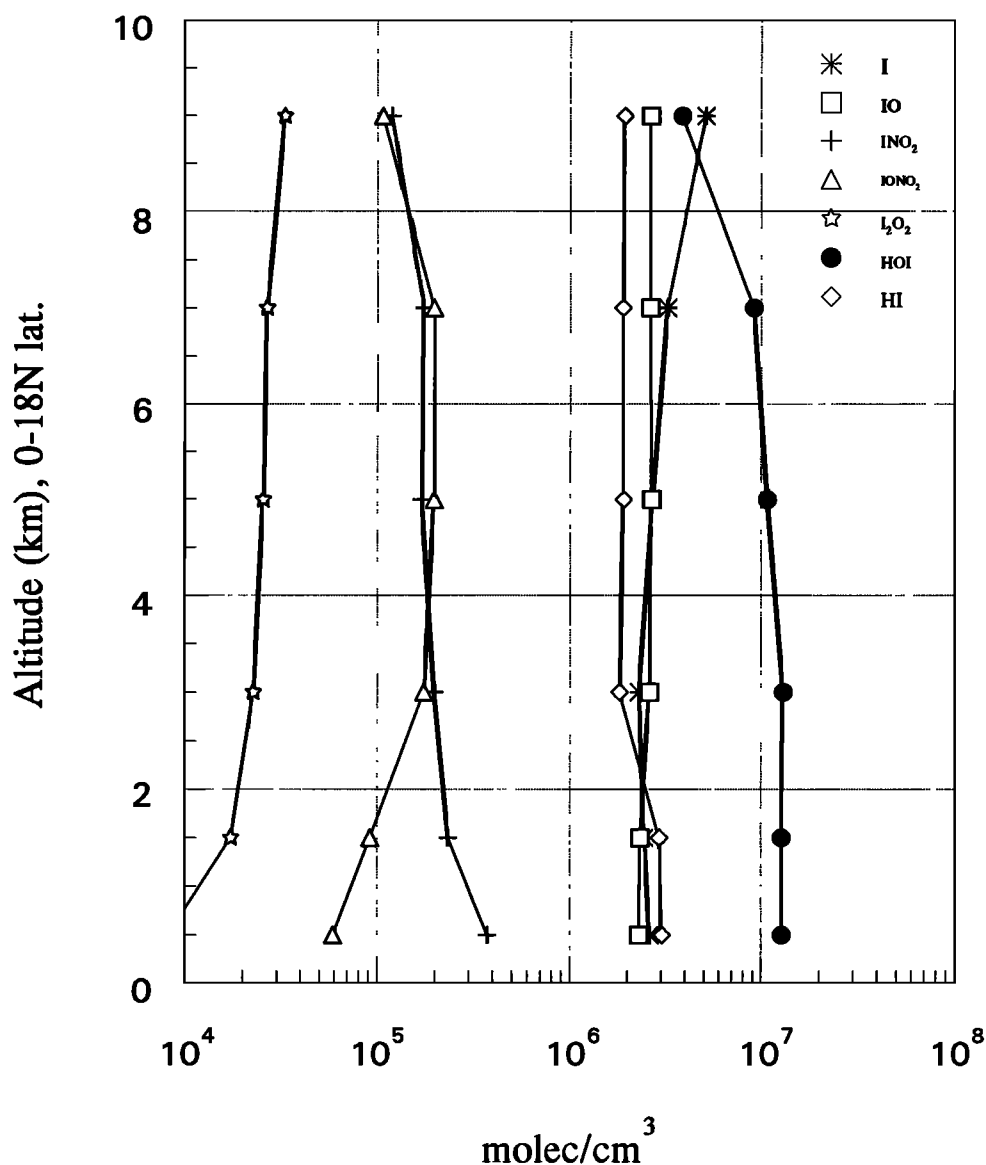


Figure 5. Altitude profiles of reactive iodine species for 0°-18°N based on the "reference" altitude trend given in Figure 2, scaled to give 1.5 pptv of  $I_x$  at high-altitude.

Solomon et al. examined the issue of aerosol sinks for iodine as related to the lower stratosphere. The chemical nature of these aerosols was taken to be predominantly sulfate and/or sulfuric acid, as are probably also aerosols for the upper troposphere. Although very little information is now available on heterogeneous reactions of iodine, Solomon and co-workers have argued from analogy with chlorine chemistry [e.g., Hanson et al., 1994] that because of the high reactivity of iodine, it would most likely not be permanently removed but would simply be recycled. Furthermore, these investigators suggest that the partitioning of iodine between the aerosol and gas phases would tend to favor most iodine being in the gas phase. However, given the impact of a 14-day aerosol sink, it would seem prudent to more fully explore the issue of heterogeneous loss of iodine.

### 3.2 Ozone Destruction

As discussed earlier in the text, the two most significant iodine-related  $O_3$  sinks involve the reaction sequences (R2),

(R8), (R14), and (R2), and (R9). Ozone destruction due to the IO self-reaction (R9) is found to be strongly dependent on both the altitude and the absolute  $I_x$  level selected. Thus only for  $I_x$  levels at 7 pptv are IO levels found to be sufficiently high that this reaction contributes greater than 10% to the total iodine-related  $O_3$  destruction; for example, see Table 2. In addition, even at 7 pptv of  $I_x$ , (R9) does not become significant until reaching altitudes >6 km. For example, from Table 2 it can be seen that only at 10 to 12 km is approximately 30% of the iodine-related  $O_3$  destruction due to the IO self-reaction.

As shown in Table 2 (top), for the case of 0.5 pptv  $I_x$  the predicted  $O_3$  destruction  $D(O_3)$  due to iodine never exceeds that estimated from  $HO_x$  alone by more than 8%. This leads to a relatively small 0 to 12-km column  $D(O_3)$  effect of only 2%. Based on what we believe to be a more typical source scenario, involving 1.5 pptv  $I_x$ , Table 2 (middle) indicates that for some altitude/latitude ranges, as much as a 24% increase in  $D(O_3)$  might occur. In all cases the general trend in  $D(O_3)$  is seen as involving increasing iodine effects with

**Table 2.** Diurnally Averaged, Column Integrated Ozone Destruction from Iodine

Latitude	Altitude	Without $I_x$ , molec/cm <sup>2</sup> /s	With .5 pptv $I_x^a$ , molec/cm <sup>2</sup> /s	%Effect
0-18	0-1	4.84E+10	4.91E+10	1.41
0-18	1-2	4.57E+10	4.65E+10	1.74
0-18	2-4	8.86E+10	9.01E+10	1.74
0-18	4-6	5.57E+10	5.72E+10	2.62
0-18	6-8	3.70E+10	3.82E+10	3.27
0-18	8-10	0.85E+10	0.91E+10	7.81
		(28.4E+10) <sup>b</sup>	(29.0+10) <sup>b</sup>	(2.24) <sup>b</sup>
18-42	0-1	5.10E+10	5.17E+10	1.31
18-42	1-2	7.69E+10	7.77E+10	1.04
18-42	2-4	9.01E+10	9.15E+10	1.57
18-42	4-6	5.98E+10	6.12E+10	2.27
18-42	6-8	2.36E+10	2.47E+10	4.46
18-42	8-10	1.33E+10	1.40E+10	5.64
18-42	10-12	0.39E+10	0.41E+10	6.81
		(31.9E+10) <sup>b</sup>	(32.5E+10) <sup>b</sup>	(1.98) <sup>b</sup>
Latitude	Altitude	Without $I_x$ , molec/cm <sup>2</sup> /s	With 1.5 pptv $I_x^a$ , molec/cm <sup>2</sup> /s	% Effect
0-18	0-1	4.84E+10	5.05E+10	4.24
0-18	1-2	4.57E+10	4.81E+10	5.22
0-18	2-4	8.86E+10	9.32E+10	5.20
0-18	4-6	5.57E+10	6.01E+10	7.84
0-18	6-8	3.70E+10	4.06E+10	9.80
0-18	8-10	0.85E+10	1.05E+10	23.81
		(28.4E+10) <sup>b</sup>	(30.3E+10) <sup>b</sup>	(6.71) <sup>b</sup>
18-42	0-1	5.10E+10	5.30E+10	3.94
18-42	1-2	7.69E+10	7.93E+10	3.11
18-42	2-4	9.01E+10	9.43E+10	4.71
18-42	4-6	5.98E+10	6.39E+10	6.82
18-42	6-8	2.36E+10	2.68E+10	13.51
18-42	8-10	1.33E+10	1.156E+10	17.44
18-42	10-12	0.39E+10	0.47E+10	21.30
		(31.9E+10) <sup>b</sup>	(33.8E+10) <sup>b</sup>	(5.98) <sup>b</sup>
Latitude	Altitude	Without $I_x$ , molec/cm <sup>2</sup> /s	With 7 pptv $I_x^a$ , molec/cm <sup>2</sup> /s	%Effect
0-18	0-1	4.84E+10	5.80E+10	20
0-18	1-2	4.57E+10	5.67E+10	24
0-18	2-4	8.86E+10	11.0E+10	24
0-18	4-6	5.57E+10	7.60E+10	36
0-18	6-8	3.70E+10	5.40E+10	46
0-18	8-10	0.85E+10	1.89E+10	123
		(28.4E+10) <sup>b</sup>	(37.3E+10) <sup>b</sup>	(32) <sup>b</sup>
18-42	0-1	5.10E+10	6.04E+10	18
18-42	1-2	7.69E+10	8.80E+10	14
18-42	2-4	9.01E+10	11.0E+10	22
18-42	4-6	5.98E+10	7.89E+10	32
18-42	6-8	2.36E+10	3.93E+10	66
18-42	8-10	1.33E+10	2.60E+10	95
18-42	10-12	0.39E+10	0.85E+10	122
		(31.9E+10) <sup>b</sup>	(41.1E+10) <sup>b</sup>	(29) <sup>b</sup>

Read 4.84E+10 as 4.84x10<sup>10</sup>.<sup>a</sup>  $I_x$  levels at all altitudes have been scaled to the "reference" curve given in Figure 3.<sup>b</sup> Column integrated numbers

increasing altitude. However, it must be recognized that this trend is strongly influenced by the rapidly decreasing contribution to  $D(O_3)$  from  $HO_x$  chemistry alone. As a result, although the percent change in  $D(O_3)$  is largest for high-altitudes, the total column effect on  $D(O_3)$  is actually more influenced by middle free tropospheric altitudes.

A similar trend in  $D(O_3)$  is seen for  $I_x$  levels of 7 pptv, e.g., Table 2 (bottom). In this case, the upper altitude values of  $D(O_3)$  are shifted by factors of 2 or more due to the inclusion of iodine chemistry. The resulting enhancement in total column  $O_3$  destruction is approximately 30%. If this evaluation of the PEM-West A tropical regime is further extended to the tropopause (based on generic high-altitude tropical trace gas compositions), we find that total  $O_3$  column destruction is increased by only an additional 2% over that cited above for 0-10 km. This result once again makes the point that although very large effects can be found from iodine at high-altitudes, these altitudes tend to contribute less to the total column  $D(O_3)$  effect.

Taking for the moment the most extreme case for the impact of iodine on the troposphere (e.g.,  $I_x$  levels of 7 pptv), the total-column  $D(O_3)$  results from Table 2 ( $8 \times 10^{10}$  molecules/cm<sup>2</sup>/s) indicate that this photochemical destruction flux would be nearly 1.5 times larger than the  $O_3$  deposition flux to the ocean [e.g., Kawa and Pearson, 1989; Lenschow *et al.*, 1982]. Equally noteworthy is the fact that, as discussed by Davis *et al.* [this issue], even before adding iodine, the PEM-West A tropical regime has been evaluated as having an imbalance between  $O_3$  photochemical production and destruction of between 3 and  $12 \times 10^{10}$  molecules/cm<sup>2</sup>/s. (The lower deficit number assumes significant high-altitude (e.g., 10-17 km) production of  $O_3$  due the presence of high levels of lightning-generated  $NO_x$ .) If, however, this region is at steady state for  $O_3$  as suggested by Davis *et al.*, [this issue, 1995] then an additional  $8 \times 10^{10}$  molecules/cm<sup>2</sup>/s  $O_3$  loss due to iodine raises still further questions concerning our level of understanding of the tropical ozone budget. Most likely, it means that during the time period of PEM-West A,  $I_x$  levels were much closer to those labeled earlier as "typical," i.e., 1.5 pptv. Quite clearly, the optimum location for seeing a maximum iodine effect was not that defined by the PEM-West A mission as evidenced by the low primary productivity levels estimated from the low observed levels of  $CH_3I$ .

### 3.3. Modulation of $HO_2/OH$ and $NO_2/NO$ Ratios

Based on (R8), (R14), and (R7), one would predict that with increasing levels of  $I_x$ , shifts should occur in both the ratios  $HO_2/OH$  and the  $NO_2/NO$ . But, as seen in Tables 3 (top) and 3 (middle) only minor changes are seen in these ratios when  $I_x$  levels are limited to 0.5 and 1.5 pptv. By comparison, for  $I_x$  levels of 7 pptv the  $HO_2/OH$  ratio is observed to shift by as much as -18 to -24%, depending on latitude and altitude. The trend in this ratio is one which shows increasing negative values with increasing altitude. The average for all altitudes and latitudes is estimated here to be -15%. This leads to an average increase in the level of OH by 9%; for example, the OH effect typically defines 60% of the total change in the  $HO_2/OH$  ratio. Given this shift in OH, if  $I_x$  levels were to persist at the 7 pptv level for an extended period of time, one would also estimate a correspondingly 9% shorter lifetime for OH-controlled long-lived trace gases such as  $CH_4$  and  $CH_3CCl_3$ .

Concerning changes in the ratio  $NO_2/NO$ , from Table 3 (bottom) it can be seen that 7 pptv of  $I_x$  shifts the value of this ratio by a maximum of 11%. Furthermore, this shift is only observed for the highest altitudes examined. The average shift over all altitudes and latitudes is approximately 5%. Thus on average, the magnitude of the iodine shift in

**Table 3.** Tropospheric Impact of Iodine on Ratios HO<sub>2</sub>/OH and NO<sub>2</sub>/NO

Latitude	Altitude	HO <sub>2</sub> /OH <sub>x</sub>	HO <sub>2</sub> /OH <sub>x</sub>	HO <sub>2</sub> /OH <sub>x</sub>	NO <sub>2</sub> /NO <sub>x</sub>	NO <sub>2</sub> /NO <sub>x</sub>	NO <sub>2</sub> /NO <sub>x</sub>
		Without I <sub>x</sub>	With 0.5 pptv I <sub>x</sub> <sup>a</sup>	% Effect <sup>b</sup>	Without I <sub>x</sub>	With 0.5 pptv I <sub>x</sub> <sup>a</sup>	% Effect <sup>b</sup>
0-18	0-1	109	108	-0.7	1.30	1.31	0.2
0-18	1-2	105	104	-0.9	1.20	1.21	0.2
0-18	2-4	78	77	-1.1	1.21	1.21	0.2
0-18	4-6	81	80	-1.4	0.87	0.88	0.2
0-18	6-8	76	75	-1.5	0.68	0.68	0.2
0-18	8-10	66	64	-2.2	0.32	0.32	0.5
18-42	0-1	91	90	-0.7	1.55	1.55	0.2
18-42	1-2	82	82	-0.7	2.00	2.00	0.1
18-42	2-4	85	84	-0.9	1.46	1.46	0.1
18-42	4-6	71	70	-1.2	1.14	1.14	0.2
18-42	6-8	64	63	-1.5	0.70	0.70	0.3
18-42	8-10	41	40	-1.5	0.47	0.47	0.5
18-42	10-12	32	32	-0.9	0.19	0.19	0.8

Latitude	Altitude	HO <sub>2</sub> /OH <sub>x</sub>	HO <sub>2</sub> /OH <sub>x</sub>	HO <sub>2</sub> /OH <sub>x</sub>	NO <sub>2</sub> /NO <sub>x</sub>	NO <sub>2</sub> /NO <sub>x</sub>	NO <sub>2</sub> /NO <sub>x</sub>
		Without I <sub>x</sub>	With 1.5 pptv I <sub>x</sub> <sup>a</sup>	% Effect <sup>b</sup>	Without I <sub>x</sub>	With 1.5 pptv I <sub>x</sub> <sup>a</sup>	% Effect <sup>b</sup>
0-18	0-1	109	106	-2.2	1.30	1.31	0.7
0-18	1-2	105	103	-2.7	1.20	1.21	0.6
0-18	2-4	78	75	-3.2	1.21	1.22	0.7
0-18	4-6	81	77	-4.0	0.87	0.88	0.6
0-18	6-8	76	73	-4.3	0.68	0.69	0.6
0-18	8-10	66	61	-6.4	0.32	0.32	1.5
18-42	0-1	91	89	-2.1	1.55	1.56	0.7
18-42	1-2	82	81	-2.1	2.00	2.01	0.4
18-42	2-4	85	83	-2.6	1.46	1.46	0.4
18-42	4-6	71	68	-3.5	1.14	1.15	0.5
18-42	6-8	64	62	-4.5	0.70	0.71	0.9
18-42	8-10	41	39	-4.3	0.47	0.48	1.6
18-42	10-12	32	31	-2.7	0.19	0.19	2.3

Latitude	Altitude	HO <sub>2</sub> /OH <sub>x</sub>	HO <sub>2</sub> /OH <sub>x</sub>	HO <sub>2</sub> /OH <sub>x</sub>	NO <sub>2</sub> /NO <sub>x</sub>	NO <sub>2</sub> /NO <sub>x</sub>	NO <sub>2</sub> /NO <sub>x</sub>
		Without I <sub>x</sub>	With 7 pptv I <sub>x</sub> <sup>a</sup>	% Effect <sup>b</sup>	Without I <sub>x</sub>	With 7 pptv I <sub>x</sub> <sup>a</sup>	% Effect <sup>b</sup>
0-18	0-1	109	98	-9.4	1.30	1.34	3.3
0-18	1-2	105	93	-11.4	1.20	1.24	2.9
0-18	2-4	78	67	-13.3	1.21	1.25	3.1
0-18	4-6	81	67	-16.5	0.87	0.90	3.2
0-18	6-8	76	63	-17.3	0.68	0.70	3.2
0-18	8-10	66	50	-24.2	0.32	0.34	7.5
18-42	0-1	91	83	-9.1	1.55	1.59	3.1
18-42	1-2	82	75	-9.2	2.00	2.04	2.1
18-42	2-4	85	76	-11.1	1.46	1.49	2.1
18-42	4-6	71	60	-14.6	1.14	1.17	2.5
18-42	6-8	64	53	-18.0	0.70	0.73	4.3
18-42	8-10	41	34	-17.2	0.47	0.50	7.4
18-42	10-12	32	29	-11.6	0.19	0.21	10.9

For reference purposes the OH levels for 0°-18°N latitude and 30° zenith angle are 3.6E+6 for 0-1 km and 3.8E+6 for 6-8 km. For all altitudes and I<sub>x</sub> levels, increases in OH contribute roughly 60% to the total change in the HO<sub>2</sub>/OH ratio.

<sup>a</sup> I<sub>x</sub> levels at all altitudes have been scaled to the "reference".

<sup>b</sup> Based on steady state modeling conditions.

this ratio does not appear to provide a satisfactory explanation for the total enhancement in NO<sub>2</sub> levels observed during PEM-West A although it might have been one of the contributing factors (for further details, see *Crawford et al.* [this issue]).

#### 4. Comparison With Previous Studies

The two most relevant tropospheric iodine modeling studies that have preceded this work have been those reported by *Chameides and Davis* [1980] and *Chatfield and Crutzen* [1990]. Chameides and Davis (C&D) only examined the

case of the marine BL but did so for a wide range of median values of CH<sub>3</sub>I. Since only the total source of iodine is important, not the specific form, we have here been able to backout the level of CH<sub>3</sub>I for BL conditions that corresponds to our high-altitude 7 pptv I<sub>x</sub> scenario. For this specific case, BL levels of CH<sub>3</sub>I would be in the range of 10 to 13 pptv. Based on this input, we find that the C&D standard model predicts an approximate 25% enhancement in D(O<sub>3</sub>) over that estimated from HO<sub>x</sub> related chemistry alone. As shown in Table 2 (bottom), this is basically the same enhancement predicted from this work (i.e., 20%) for BL conditions in the tropics. Although this agreement appears to be quite good,

it turns out that it is actually quite fortuitous. For example, on closer inspection one finds that C&D estimated IO levels are nearly 1 order of magnitude higher than those estimated in this work. As a result, both the IO self-reaction and the reaction with  $\text{HO}_2$  are found to contribute significantly to  $\text{D}(\text{O}_3)$ . The reason for C&D's high IO levels now appears to be largely due to a major difference in the assignment of  $k$  values to the three critical processes (R6), (R8), and (R9). All three processes represent loss reactions for IO; and all three have now been assigned new  $k$  values based on more reliable kinetic and photochemical data. The new values are nearly 1 order of magnitude higher than the C&D values.

Chatfield and Crutzen [1990] (C&C) also explored the question of tropospheric destruction of ozone by iodine although the main thrust of the study of these investigators was the possible impact of iodine on the oxidation of marine DMS. These authors concluded that iodine was probably an insignificant sink for ozone; however, this conclusion, was based on BL  $\text{CH}_3\text{I}$  levels of only 3 pptv. In addition, C&C based their assessment on a  $k$  value for (R8) which has recently been reevaluated based on new kinetic data as being  $1\frac{1}{2}$  orders of magnitude higher [DeMore *et al.*, 1994]. The  $J$  value for (R16) was also taken to be nearly 3 orders of magnitude lower than that estimated here. All 3 factors have been found to significantly minimize the tropospheric effects of iodine. This point was demonstrated here by carrying out simulations using PEM-West A median values for all photochemical species but invoking the C&C  $\text{CH}_3\text{I}$ , (R8), and (R16) values. The  $\text{D}(\text{O}_3)$  results in this case were within a factor of 1.5 of C&C, thus agreeing with the C&C evaluation in showing no significant effect on ozone from iodine chemistry.

As noted above, the availability of new kinetic data was the basis for the  $k$  value assigned to (R8) in this study. However, in the case of (R16) no spectroscopic data are available from which to evaluate this  $J$  value [Sander, 1986; Jenkin, 1993]. C&C assumed values ranging from  $3 \times 10^{-4}$  to  $2 \times 10^{-5} \text{ s}^{-1}$ , but this is 2 orders of magnitude lower than the  $J$  value calculated from the recently reported absorption spectrum for  $\text{Cl}_2\text{O}_2$  [DeMore *et al.*, 1994]. We have taken what we believe is a rather conservative value for (R16),  $9 \times J(\text{Cl}_2\text{O}_2)$  which is approximately 3 orders of magnitude greater than C&C. This estimate is still 1 order of magnitude lower than the  $J$  value for (R6), involving the photolysis of IO.

## 5. Summary and Conclusions

The  $\text{CH}_3\text{I}$  observations from PEM-West A, in conjunction with updated  $J$  and  $k$  values for several tropospheric iodine reactions, suggest that under certain conditions the addition of iodine chemistry to current models leads to predicted enhancements in the rate of destruction of ozone. It also predicts shifts in the critical free radical ratio  $\text{HO}_2/\text{OH}$ . Although the percent effect on  $\text{D}(\text{O}_3)$  was found to increase steadily with increasing altitude, the mid-troposphere was found to be the major contributor to the 0 to 12 km column-integrated value of  $\text{D}(\text{O}_3)$ . The total column effect on  $\text{D}(\text{O}_3)$  was estimated to be only 6% for  $I_x$  levels of 1.5 pptv; however, this increased to 30% at tropical latitudes for the high  $I_x$  scenario involving 7 pptv. A potential enhancement in  $\text{D}(\text{O}_3)$  of 30% represents a major impact on the  $\text{O}_3$  budget at tropical latitudes. In fact, it is difficult to reconcile with

the findings of Davis *et al.* [this issue] who report that for the time period of PEM-West A this region displayed significant net-photochemical column destruction even in the absence of iodine chemistry. This most likely suggests that during PEM-West A,  $I_x$  never reached the 7 pptv level. This conclusion would seem to be in agreement with the observations that BL levels of  $\text{CH}_3\text{I}$  were also low indicating a marine region having low primary productivity.

The influence of iodine on the radical ratio  $\text{HO}_2/\text{OH}$  was found to be most significant for the upper free troposphere and for  $I_x$  levels of 7 pptv. For this  $I_x$  level the average effect for all altitudes was approximately 15%. The effect of iodine on the  $\text{NO}_2/\text{NO}$  ratio was also found to maximize at high-altitude but never exceeded 11% even for the highest  $I_x$  scenario. If the maximum estimated shift in the  $\text{HO}_2/\text{OH}$  ratio were to be realized, this would result in a 9% increase in atmospheric levels of OH and thus lead to an approximate 9% decrease in the lifetimes of OH-controlled trace gases such as  $\text{CH}_4$  and  $\text{CH}_2\text{CCl}_3$ .

Of interest also is the fact that median levels of  $\text{CH}_3\text{I}$  in the 8-10 km altitude range (e.g., for the western tropical Pacific) reached 0.15 pptv, with individual observations reaching 0.3 to 0.7 pptv. Although these altitudes are still significantly removed from the tropical tropopause, if the mixing ratios observed for  $\text{CH}_3\text{I}$  represent only a fraction of the total iodine being convectively pumped into the upper troposphere, it is still possible that Solomon *et al.*'s [1995] requirement of a few tenths of one pptv of iodine in the lower stratosphere might be reached on some occasions. In this context, because of the high sensitivity for detection of iodine species like  $\text{CH}_3\text{I}$ , together with its short lifetime of 2-4 days,  $\text{CH}_3\text{I}$  would appear to be an excellent tracer for the transport of marine BL air into the upper troposphere and lower stratosphere.

Major uncertainties in the proposed iodine chemistry include the total marine iodine source strength as well as the reliability of several  $k$  and  $J$  values. In particular, it will be important in future field studies to include not only measurements of  $\text{CH}_3\text{I}$  but also those for other iodocarbons. In addition, both the critical IO reaction involving  $\text{HO}_2$  (R8) and the self-reaction (R9) should be further investigated, as should the photochemical cross section for the species  $\text{I}_2\text{O}_2$ . Finally, the efficiency for removal of iodine species due to high-altitude aerosol must be resolved. Quite significant to gaining more direct insight into all aspects of the proposed iodine chemistry would be direct observations of the radical species I and IO.

**Acknowledgments.** This work was supported in part by funds from the National Aeronautics and Space Administration under grants NCC-1-148 and NAG-1438 and by the Atmospheric Chemistry Project of the Climate and Global Change Program of the National Oceanic and Atmospheric Administration. The author D. D. Davis would also like to thank the project office at NASA Langley Research Center as well as the flight crews at NASA Ames Research Center for their strong support of the PEM-West A field program. Finally, he would like to acknowledge many helpful discussions with William Chameides and Hanwant Singh.

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(Received July 8, 1995; revised August 28, 1995; accepted August 29, 1995.)